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On Equilibrium in the System: Ferrous Carbonate, Carbon Dioxide and Water

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Equilibrium between Alkali-Earth Carbonates, Carbon Dioxide and Water

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL
OF SCIENCE IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By Herbert Johnson Smith

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Reprinted from
The Journal of the American Chemical Society
Vol. XL, No. 6, June, 1918

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ON EQUILIBRIUM IN THE SYSTEM: FERROUS CARBONATE, CARBON DIOXIDE AND WATER.

It has long been known that ferrous carbonate is more soluble in water containing carbon dioxide than in pure water.[1] The increase in solubility is due to the formation of the more soluble ferrous bicarbonate, which has, however, never been obtained in the solid state. It is shown in this paper that the solid salt, at a temperature of 25°, would have a decomposition tension of carbon dioxide greater than 25 atmospheres.

If we study the system: ferrous carbonate, carbon dioxide and water

[1] Wagner, *Z. anal. Chem.*, **6**, 171 (1867); Hauer, *J. prakt. Chem.*, **81**, 381 (1860).

from the standpoint of the ionic theory and the law of mass action, we find that a certain quantitative relation must exist between the concentration of the dissolved ferrous salt and concentration of the carbon dioxide in solution.

The following 5 equations govern the equilibrium:

$$[H^+] \times [HCO_3^-] = K_1 \times [H_2CO_3] \quad (1)$$

$$[H^+] \times [CO_3^{--}] = K_2 \times [HCO_3^-] \quad (2)$$

$$[Fe^{++}] \times [CO_3^{--}] = K_3 \text{ (The solubility product constant)} \quad (3)$$

$$[HCO_3^-] = 2[Fe^{++}] \quad (4)$$

$$\alpha \times [Fe(HCO_3)_2] = [Fe^{++}] \quad (5)$$

where α is the degree of ionization of the ferrous bicarbonates.

Dividing Equations 1 by 2 we get

$$\frac{[HCO_3^-]^2}{[CO_3^{--}]} = \frac{K_1}{K_2} \times [H_2CO_3]. \quad (6)$$

Multiplying (6) by (3) we have

$$[HCO_3^-]^2 \times [Fe^{++}] = \frac{K_1K_3}{K_2} [H_2CO_3]. \quad (7)$$

But since from (4) $2[Fe^{++}] = [HCO_3^-]$ we have

$$\frac{[Fe^{++}]}{\sqrt[3]{[H_2CO_3]}} = \sqrt[3]{\frac{K_1K_3}{4K_2}} \text{ and since } [Fe^{++}] = \alpha \times [Fe(HCO_3)_2], \quad (8)$$

we have finally

$$\frac{\alpha \times [Fe(HCO_3)_2]}{\sqrt[3]{[H_2CO_3]}} = \sqrt[3]{\frac{K_1K_3}{4K_2}} = K \quad (9)$$

where K is the equilibrium constant for the system.

No quantitative data can be found in the literature for testing the applicability of Equation 9. However, Stieglitz[1] and McCoy and Smith[2] have applied a similar expression to measurements on the solubility of calcium carbonate in carbonated waters, and have shown that a good equilibrium constant is thereby obtained.

In Table I are given the results of some experiments which I have carried out on equilibrium in the system: ferrous carbonate, carbon dioxide and water.

The ferrous carbonate used was prepared according to the following method: Equimolecular quantities of solid ferrous sulfate and sodium bicarbonate were placed in a steel bottle. The air was displaced from the bottle by a stream of carbon dioxide. Water previously saturated with carbon dioxide was added. The bottle was then closed by a plug carrying a needle valve and carbon dioxide was added from a cylinder of compressed gas until a pressure of 400 pounds had been attained in

[1] *Carnegie Inst. Publication*, **107**, 233 (1909).

[2] *J. Am. Chem. Soc.*, **33**, 468 (1911).

the bottle. The valve was then closed, and the bottle kept at a temperature of 100° for several days. The ferrous carbonate obtained in this way is pure white.

The precipitate was filtered in an atmosphere of carbon dioxide and washed with water previously saturated with the gas. The precipitate is much more easily filtered and washed than one obtained by precipitation in open vessels. According to Senarmont[1] the crystals obtained by the above procedure are isomorphous with calcite and similar to the mineral siderite.

From 50 to 100 g. of the ferrous carbonate were placed in the steel bottle described by McCoy and Smith.[2] One liter of water was added, and carbon dioxide admitted through the needle valve from a cylinder of the liquefied gas. A pressure gauge afforded a means for determining the approximate pressure of the gas within the bottle. The bottle was rotated in a thermostat at 30° for several days until a state of equilibrium had been reached. Preliminary experiments showed that one week's rotation was sufficient for this.

When equilibrium had been finally attained within the bottle, the concentrations of the dissolved ferrous salt and of the carbon dioxide in solution were determined. The portion of the solution used for the analysis was withdrawn from the bottle through a brass tube packed with cotton. This tube was attached to the valve on the inside of the bottle. For the carbon dioxide determination the filtered portion was received in a tared and evacuated flask containing a few cc. of conc. sulfuric acid. The gas was removed from the flask by a stream of carbon dioxide-free air, and dried by passing through conc. sulfuric acid and over phosphorus pentoxide. It was finally absorbed in weighed Fleming towers filled with soda-lime and phosphorus pentoxide. It will be noted that in this way all of the carbon dioxide, both free and combined, is evolved. Since the iron exists in solution as the bicarbonate, the free carbon dioxide is easily obtained by subtracting from the total twice the concentration of the iron. All concentrations must be expressed, of course, in gram molecules per liter. The portion used for the iron analysis was boiled with nitric acid to oxidize the iron. The iron was next precipitated as ferric hydroxide, the precipitate washed with boiling water and redissolved in dil. sulfuric acid. The iron was then reduced to the ferrous state, using amalgamated zinc. Finally, the iron was determined by titration with seventieth normal potassium permanganate.

In the first column of Table I are given the concentrations of free carbonic acid in gram molecules per liter. The second column gives the corresponding concentrations of the ferrous bicarbonate in gram

[1] *Compt. rend.*, **28**, 693 (1849).

[2] *J. Am. Chem. Soc.*, **33**, 468 (1911).

molecules per liter. The third column gives the assumed degrees of ionizations of the ferrous bicarbonate. These ionizations I have assumed to be the same as for barium nitrate solutions of equivalent concentrations. The ionization values for barium nitrate are those given by Noyes and Melcher.[1] In the fourth column are given values for K, the equilibrium constant for the system. These values are obtained from Equation 9, using the data in Cols. 1, 2 and 3 of the table.

TABLE I.—SOLUBILITY OF FERROUS BICARBONATE IN CARBONATED WATER AT 30°.

1. (H_2CO_3).	2. $Fe(HCO_3)_2$.	3. α.	4. $K \times 10^3$.
0.1868	0.00245	0.912	3.91
0.1985	0.00256	0.909	3.99
0.2168	0.00262	0.908	3.96
0.2327	0.00274	0.907	4.04
0.2960	0.00303	0.902	4.10
0.3116	0.00304	0.902	4.04
0.3153	0.00318	0.898	4.19
0.3294	0.00311	0.900	4.05
0.3745	0.00315	0.898	3.93
0.4046	0.00332	0.896	4.02
0.4750	0.00348	0.893	3.98
0.6600	0.00402	0.884	4.08
0.7154	0.00418	0.880	4.11
0.7600	0.00434	0.878	4.18
			Av., 4.04

Rearrangement of Equation 9 gives

$$[Fe^{++}] \times [CO_3^{--}] = K_3 = \frac{4K_2K^3}{K_1}. \qquad (10)$$

We see that, given the values of K_1 and K_2, we can calculate the value of K_3, since K is now known.

The value of K_1, the first ionization constant of carbonic acid, was first accurately determined by Walker and Carmack.[2] They found K_1 to equal 3.04×10^{-7} at 18°. A more recent, and perhaps a slightly more accurate, value has been obtained by Kendall.[3] He found K_1 to equal 3.12×10^{-7} at 18°. Kendall also determined values for K_1 at 0° and at 25°. Assuming that the value increases at the same rate between 25 and 30° as it does between 0 and 25°, we get a value for K_1 of 3.75×10^{-7} at 30°.

The best value for K_2, the second ionization constant for carbonic acid, has been obtained by Seyler and Lloyd.[4] The calculation of K_2 from their experimental data involves a knowledge of K_1 and of K_w (ion product

[1] *Carnegie Inst. Publication*, **63**, 108 (1907).
[2] *J. Chem. Soc.*, **77**, 8 (1900).
[3] *J. Am. Chem. Soc.*, **38**, 1480 (1916).
[4] *J. Chem. Soc.*, **111**, 138 (1917).

constant for water). Using Kendall's value for K_1 at 25° and taking K_w equal to 0.82×10^{-14}, they obtained 4.91×10^{-11} as the value of K_2 at 25°. No experimental data are known from which the variation of K_2 with temperature can be determined.

If, in Equation 10 we substitute 3.75×10^{-7} for K_1; 4.91×10^{-11} for K_2; and $4.04 \times 10^{-}$ for K, we get K_3 equal to 34.53×10^{-12}. Then if ferrous carbonate were not hydrolytically dissociated, its solubility in pure water free from carbon dioxide would be 5.8×10^{-6} gram molecules per liter.

ON EQUILIBRIUM IN THE SYSTEM: ZINC CARBONATE, CARBON DIOXIDE AND WATER.[1]

When zinc salts in solution are precipitated by alkaline carbonates, the compounds produced are apparently unstable and of variable composition. A large number of basic zinc carbonates have been described in the literature. It has been shown, however, by Mikusch[2] that there exist only 2 carbonates of zinc. One is the normal zinc carbonate, $ZnCO_3$; the other is a basic zinc carbonate whose composition is expressed by the formula $5ZnO.2CO_2.4H_2O$. All other basic zinc carbonates described in the literature are shown to be solid solutions of zinc hydroxide and neutral zinc carbonate.

It has been shown by Free[3] that the solubility of basic copper carbonate increases with the concentration of free carbon dioxide. Seyler[4] points out that Free's results exhibit regularities similar to those found for other carbonates. Seyler deduces these regularities from the principles of chemical equilibrium and shows experimentally that they apply to the solubility of basic zinc and lead carbonates. No previous experimenters have examined the equilibrium between normal zinc carbonate, carbon dioxide, and water for pressures of carbon dioxide greater than one atmosphere. In view of this fact, I have undertaken a study of this system under high pressures.

The theory of this equilibrium from the standpoint of the law of mass action and the ionic theory is similar to that deduced for the system: ferrous carbonate, carbon dioxide and water. This is given in the preceding paper. Since the valence of zinc ion is the same as that of the fer-

[1] From a dissertation submitted to the Faculty of the Ogden Graduate School of Science of the University of Chicago in candidacy for the Degree of Doctor of Philosophy.

[2] *Z. Phys. Chem.*, **56**, 367 (1906).

[3] *J. Am. Chem. Soc.*, **30**, 1366 (1908).

[4] *Analyst*, **33**, 756 (1908).

rous ion, an equation similar to (9) of that paper should hold for the zinc equilibrium.

The zinc carbonate used in these experiments was prepared from the purest commercially obtainable zinc carbonate by washing repeatedly with large quantities of boiling water. The basic zinc carbonate thus obtained was placed with water in a steel bottle and carbon dioxide was added until a pressure of 30 atmospheres was reached. The steel bottle was rotated in a thermostat at 25° for several days.

About 50 g. of the zinc carbonate thus prepared was placed in a steel bottle. The bottle was then nearly filled with water and closed with a plug carrying a needle valve, through which it was charged with carbon dioxide from a cylinder of the liquefied gas. The inside of the bottle was protected from the action of the carbonic acid by a coating of beeswax applied hot. The cylinder and bottle were then rotated in a thermostat for several days until equilibrium had been reached. Preliminary experiments showed that about one week's rotation was necessary for this.

The solution was then analyzed for dissolved zinc salt and carbon dioxide. In this case the zinc was determined by adding to a weighed portion of the solution an excess of 0.05 *N* hydrochloric acid, boiling to remove all carbon dioxide, cooling, adding one drop of methyl orange, and titrating the excess of acid with 0.05 *N* barium hydroxide. This method of analysis is described by Kantor and Benedikt.[1] Preliminary experiments carried out with known weights of zinc showed it to be accurate. The carbon dioxide was determined as described in the accompanying paper on ferrous carbonate.

In Table I are given the results of experiments carried out at 25°. Table II gives results at a temperature of 30°. Col. 1 gives concentration of free carbonic acid in gram molecules per liter. Col. 2 the concentrations of zinc bicarbonate in gram molecules per liter. Col. 3 gives the degrees of ionization of the zinc bicarbonate. It is assumed that the bicarbonate is ionized to the same extent as zinc chloride solutions of equivalent concentrations. The ionization of the zinc chloride solutions are calculated from the data given in Kohlrausch's *Leitervermögen der Elektrolyte*, 1st Edition, p. 160 (1898). Col. 4 gives the values of the equilibrium constant calculated from the equation

$$\frac{\alpha \times [Zn(HCO_3)_2]^2}{\sqrt[3]{[H_2CO]}} = \sqrt[3]{\frac{K_1K_3}{4K_2}} = K.$$

In the fifth column are given the pressures of the carbon dioxide. These pressures were not actually measured, but were calculated on the assumption that Henry's law holds for high pressures of the gas. The solubility of the gas in pure water at 25° under one atmosphere is given by Geffcken[2]

[1] *Z. angew. Chem.*, 1888, p. 236.

[2] Geffcken, *Z. phys. Chem.*, 49, 273 (1904).

as 0.03374 gram molecules per liter. However, these calculated pressures are lower than the actual pressures, as it is well known that Henry's law does not apply under these high pressures.

TABLE I.—SOLUBILITY OF ZINC CARBONATE IN CARBONATED WATER AT 25°.

1. $[H_2CO_3]$.	2. $[Zn(HCO_3)_2]$.	3. α.	4. $K \times 10^3$.	5. Atmospheres pressure.
0.1390	0.00194	0.909	3.40	4.12
0.1797	0.00211	0.905	3.39	5.33
0.2579	0.00242	0.899	3.41	7.64
0.3580	0.00270	0.894	3.40	10.61
0.4103	0.00278	0.894	3.35	12.16
0.4480	0.00291	0.892	3.39	13.29
0.6657	0.00317	0.888	3.22	19.73
0.6969	0.00319	0.888	3.20	20.65
0.7610	0.00343	0.885	3.33	22.56
1.3701	0.00445	0.871	3.48	40.61
			Av., 3.36	

TABLE II.—SOLUBILITY OF ZINC CARBONATE IN CARBONATED WATER AT 30°.

1. $[H_2CO_3]$.	2. $[Zn(HCO_3)_2]$.	3. α.	4. $K \times 10^3$.
0.1838	0.00215	0.904	3.42
0.3838	0.00277	0.894	3.41
0.4038	0.00286	0.892	3.41
0.4601	0.00308	0.889	3.55
0.6064	0.00324	0.888	3.40
0.6257	0.00337	0.886	3.49
0.7470	0.00352	0.884	3.43
0.8351	0.00376	0.880	3.51
1.0840	0.00339	0.878	3.41
1.1275	0.00429	0.874	3.60
			Av, 3.47

Since $$K = \sqrt[3]{\frac{K_1 K_3}{4K_2}} \quad \text{or} \quad K_3 = \frac{K^3 . K_{42}}{K_1}$$

it is possible to calculate K_3, the solubility product constant of zinc carbonate. Substituting $K = 3.36 \times 10^{-3}$, $K_1 = 3.50 \times 10^{-7}$ and $K_2 = 4.91 \times 10^{-11}$, we find $K_3 = 21 \times 10^{-12}$ at 25°.

If zinc carbonate were not hydrolytically dissociated, its solubility in pure water at 25° would be 4.58×10^{-6} gram molecules per liter.

EQUILIBRIUM BETWEEN ALKALI-EARTH CARBONATES, CARBON DIOXIDE AND WATER.

In view of the importance of an accurate knowledge of the state of equilibrium between calcium carbonate, carbon dioxide and water and the fact that previous experimenters[1] had not used modern physico-chemical methods, nor carried the measurements to higher pressures than 6 atmospheres, we undertook a study of the system in question.

As is well known, the concentration of dissolved lime increases with increasing concentration of carbonic acid. The theory of the equilibrium has been treated by van't Hoff,[2] Bodländer[3] and Stieglitz.[4]

The following fundamental equations govern the equilibrium:

(1) $H \times HCO_3 = k_1 \times H_2CO_3.$

(2) $H \times CO_3 = k_2 \times HCO_3.$

(3) $Ca \times CO_3 = k_3$, the solubility product.

(4) $HCO_3 = 2Ca.$

(5) $Ca = \alpha \times Ca(CHO_3)_2.$

If k is the equilibrium constant for reaction,

(6) $$\frac{\alpha \times Ca(HCO_3)_2}{\sqrt[3]{H_2CO_3}} = \sqrt[3]{\frac{k_1 k_3}{4k_2}} = k.$$

Bodländer showed that Schloessing's experiments gave a good equilibrium constant and calculated k_3, the solubility product of calcium carbonate, from the results. The value found is erroneous[5] owing to the use of an incorrect value for the secondary ionization constant of carbonic acid. Stieglitz has made a critical recalculation of the solubility product from Schloessing's experiments and other available data giving k_1 and k_2. Seyler and Lloyd[6] have also studied the problem under conditions applicable to geological problems.

In our experiments, for partial pressures of carbon dioxide, less than

[1] Schloessing, *Compt. rend.*, **74**, 1552; **75**, 70 (1872); Engler, *Ann. chim. phys.*, [6] **13**, 348 (1888); Seyler and Lloyd, *J. Chem. Soc.*, **95**, 1347 (1909).

[2] *Z. physik. Chem.*, **1**, 505 (1887).

[3] *Ibid.*, **35**, 23 (1900).

[4] *Carnegie Inst. Publication*, **107**, 233 (1908).

[5] Stieglitz, *Loc. cit.* McCoy, *Am. Chem. J.*, **29**, 437 (1903).

[6] *Loc. cit.*

one atmosphere, 500 cc. glass bottles were used. For higher pressures we used a 2 liter seamless, pressed steel bottle with a needle valve, capable of withstanding the pressure of liquid carbon dioxide. The inside of the bottle was effectively protected from the action of the carbonic acid by a thin coating of a mixture of beeswax and Venice turpentine, applied hot. The calcium carbonate used was made by precipitating pure calcium nitrate with ammonium carbonate at 15° and washing the precipitate free from ammonium nitrate. By working in the cold the calcite variety was obtained.

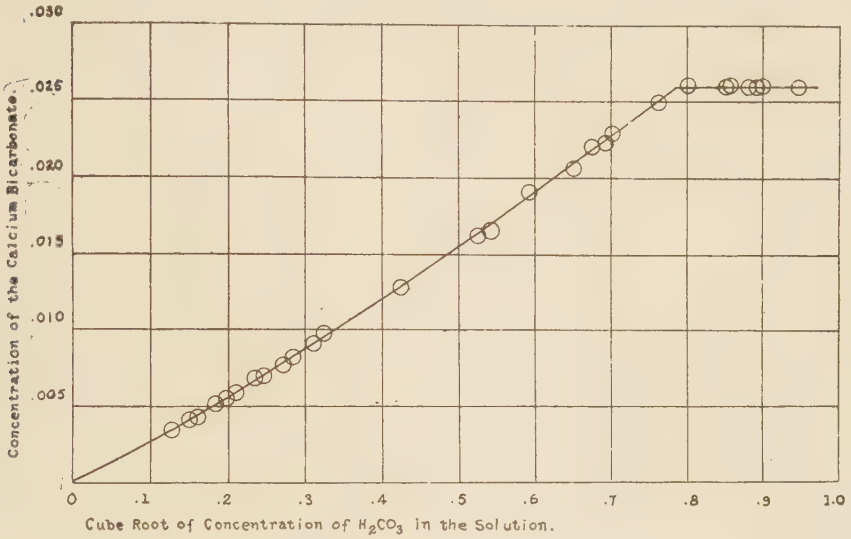
The glass bottles were charged with about 50 g. of calcium carbonate and 250 cc. of water; the steel bottle with about double these quantities. Carbon dioxide was then introduced in the desired amount. For experiments at greater than atmospheric pressure the gas was drawn from a steel cylinder of liquid carbon dioxide. The charged bottles were rotated in a thermostat at 25° + 0.02 for from 2 to 3 days, in which time equilibrium was reached. At low pressures the bottles were allowed to stand in the thermostat until the solution became clear. Portions of the latter were then removed by a pipet and analyzed. For high pressures, a brass tube, 1 × 5 cm., filled with cotton and attached to the inside of the needle valve of the steel bottle, served to filter the solution. Suitable portions of the filtered solution were drawn off into tared, evacuated, round-bottomed flasks. For the carbon dioxide analysis, the flask contained a solution of barium chloride and a known volume of standard potassium hydroxide, so that, although the carbonate solution gave off gaseous carbon dioxide as soon as the pressure was released, none of the gas was lost. The amount of solution taken for analysis was determined by weight and the excess of alkali titrated with 0.05 N hydrochloric acid, using phenolphthalein as indicator.[1] In the analysis for calcium the solution was run into a dry flask and although it became supersaturated with $CaCO_3$, owing to loss of CO_2, it remained clear for a sufficient time to prevent deposition of $CaCO_3$ in the valve or connecting tube. The solution was weighed and then titrated with $N/20$ HCl, using methyl orange as indicator.

The results of the experiments are shown in the accompanying graph, where the ordinates are molecular concentrations of $Ca(HCO_3)_2$ and the abscissas cube roots of molecular concentrations of free H_2CO_3, all free carbon dioxide in the solution being calculated as H_2CO_3. A few nearly coinciding points have been omitted. Fifteen experiments were made in glass bottles at pressures of carbon dioxide between 0.06 and 1 atmosphere. Twenty-one experiments were made in the steel bottle at pressures between 2 and 25 atmospheres. These values are not actual measured pressures but are those calculated from the solubility at atmospheric

[1] Winkler's method, see Küster, *Z. anorg. Chem.*, **13**, 127 (1897).

pressure[1] by Henry's law, which, however, does not apply closely for carbon dioxide as shown by Wroblewski.[2]

As shown by the graph, a maximum solubility of calcium salt is reached at a certain concentration of carbonic acid. This is 0.485 normal molecular and corresponds to a calculated carbon dioxide pressure of about



15 atmospheres. The obvious interpretation is that the solution becomes saturated with $Ca(HCO_3)_2$ at this point. This saturated solution is 0.026 molecular, equal to 0.42 g. of $Ca(HCO_3)_2$ per 100 cc. Theoretically it should be possible to convert all of the solid $CaCO_3$ present (about 100 g.) into solid bicarbonate by introducing carbon dioxide in sufficient amount at a pressure greater than 15 atmospheres. As long as any solid $CaCO_3$ remained the pressure of carbon dioxide should finally fall to 15 atmospheres. It was found, however, that pressures between 16 and 25 atmospheres remained at the end of 2 or 3 days' rotation of the steel bottle and that the solid residue was still largely, if not wholly, $CaCO_3$. This would seem to show that our interpretation is incorrect. But when we consider that about 2 days are required to dissolve the 2 g. of $CaCO_3$ necessary to saturate the solution at its maximum concentration, we could not expect to accomplish the complete conversion of the CO_2 and $CaCO_3$ into bicarbonate in less than 3 months. We are inclined to think, therefore, that when we can give the reaction sufficient time we shall find the facts in harmony with the hypothesis.[3] This hypothesis is also

[1] Just, *Z. physik. Chem.*, **37**, 342 (1901); Geffcken, *Ibid.*, **49**, 273 (1904).

[2] *Compt. rend.*, **94**, 955, 1355 (1882).

[3] This investigation had to be discontinued in Aug., 1910. We hope to resume it in the near future.

supported by the experiments of Keiser[1] who found that an unstable precipitate was formed by the action of NH_4HCO_3 on a cold solution of $CaCl_2$. The precipitate had the approximate composition $CaCO_3 1.75 H_2CO_3$ and was evidently impure calcium bicarbonate. It is now easy to explain why the precipitate decomposed so readily: its decomposition pressure was much greater than 1 atmosphere.

The numerical results of 6 typical experiments of the 36 completed are given in the following table:

Approx. pres. CO_2 in atmos.	1000 H_2CO_3.	1000 $Ca(HCO_3)_2$.	100 α.	1000 k.
0.1	3.522	4.116	86.6	23.4
1.1	37.28	9.734	81.0	23.6
9.9	332.9	22.36	72.8	23.5
13.2	444.0	24.95	71.3	23.3
16.3	550.0	26.00	..	..
25.4	858.0	26.03	..	..

The calculated approximate pressures are not to be considered as accurate. The concentrations of H_2CO_3 and $Ca(HCO_3)_2$ were found by analysis as described. In the fourth column, α is the assumed degree of ionization of $Ca(HCO_3)_2$, which is taken to be the same as that of calcium acetate at the same concentration, the values given having been calculated from the figures given by Kohlrausch and Holborn,[2] p. 161. The equilibrium constant k was calculated by Equation 6.

$$k = \frac{\alpha \times Ca(HCO_3)_2}{\sqrt[3]{H_2CO_3}}.$$

The mean value of k for the 29 experiments at pressures less than 15 atmospheres, where the solutions were unsaturated with $Ca(HCO_3)_2$, was 0.0234; the maximum was 2.5 per cent. higher; the minimum was 2.5 per cent. lower; the average deviation from the mean was 1.0 per cent. The 7 experiments at pressures greater than 15 atmospheres all gave essentially identical concentrations of $Ca(HCO_3)_2$. This fact is illustrated by the last two results given in the table and is clearly shown by the graph. Naturally, these 7 experiments may not be used to calculate the equilibrium constant. Seyler and Lloyd's experiments on the solubility of $CaCO_3$ in aqueous carbonic acid were made at "room temperature." Their equilibrium constant, F, bears to ours the relation

$$k = 0.02\sqrt[3]{F}.$$

Their average value of $F = 113$ substituted in the above equation gives $k = 0.0242$; our own experiments gave 0.0234.

In Equation 6 k_3, the solubility product of $CaCO_3$, is expressed in terms of k, the equilibrium constant determined by this investigation and k_1

[1] *J. Am. Chem. Soc.*, **30**, 1711 (1908).

[2] Leitvermögen, Leipzig, 1898.

and k_2, the primary and secondary ionization constants of carbonic acid. Rearrangement of (6) gives

(7) $$Ca \times CO_3 = k_3 = 4k_2k^3/k_1.$$

The constant k_1 was determined by Walker and Carmack[1] by conductivity measurements to be 3.04×10^{-7}. The secondary constant, k_2, is not known with the same degree of accuracy as k_1. Experiments by one of us[2] on the equilibrium between Na_2CO_3, $NaHCO_3$, CO_2 and H_2O give the only available data for the calculation of k_2. From the results with 0.1 N solutions, the original calculation gave the value $k_2 = 6.04 \times 10^{-11}$. The subsequent work of Geffcken[3] on the effect of salts on the solubility of carbon dioxide gave data from which Stieglitz corrected the calculation and found $k_2 = 6.20 \times 10^{-11}$. For some unknown reason, more concentrated sodium carbonate solutions gave considerably higher values: for 0.3 N solutions $k_2 = 7.8 \times 10^{-11}$. Normal solutions gave still higher values. Extrapolation gives $k_2 = 5.4 \times 10^{-11}$ for an infinitely dilute solution and 5.5×10^{-11} for a solution 0.02 N. As the solutions of $Ca(HCO_3)_2$ were from 0.003 to 0.026 N we shall use in the following calculations $k_2 = 5.5 \times 10^{-11}$. Substitution of this value in Equation 7 gives $k_3 = 9.3 \times 10^{-9}$. Stieglitz used $k_2 = 7 \times 10^{-11}$ and obtained from Schloessing's experiments $k_3 = 12.6 \times 10^{-9}$. If we use the same value of k_2, our experiments give $k_3 = 11.9 \times 10^{-9}$. We think that the lower value of k_2, and therefore also of k_3, is preferable. Seyler and Lloyd point out that k_2, the secondary constant for carbonic acid, decreases with decreasing concentration of the sodium carbonate solutions used in its determination by McCoy's method. For this reason they did not try to calculate the solubility product of $CaCO_3$. They have undertaken a new determination of k_2 but the results are apparently not yet published.

If $CaCO_3$ were not hydrolytically dissociated, the concentration of Ca (equal also to CO_3) in pure water, free from CO_2, would be $k_3 = 9.6 \times 10^{-5}$ or 9.6 mg. per liter. It is now possible to calculate the concentrations of the components of such a solution, when hydrolytic dissociation is taken into account. In addition to Equations 1, 2 and 3 the following relations also exist:

(8) $$H \times OH = k_w$$

(9) $$H + 2Ca = OH + HCO_3 + 2CO_3,$$

since the solution is electrically neutral. This reduces to

(10) $$2Ca = OH + HCO_3 + 2CO_3$$

by reason of the negligibly small value of H compared with $2Ca$.

[1] *J. Chem. Soc.*, **77**, 5 (1900).
[2] McCoy, *Loc. cit.*
[3] *Loc. cit.*

Finally,

$$Ca = HCO_3 + CO_3 + H_2CO_3 \tag{11}$$

if there is no excess or deficiency of CO_2. The six equations give

$$\frac{H^4(2H + k_1)^2}{H^2 + k_1H + k_1k_2} = \frac{k_1k_2k_w^2}{k_3}. \tag{12}$$

The solution of (12) gives $H = 1.09 \times 10^{-10}$, from which we then find $Ca = 1.66 \times 10^{-4}$; $CO_3 = 0.56 \times 10^{-4}$; $H_2CO_3 = 1.10 \times 10^{-4}$; $OH = 1.10 \times 10^{-4}$; $H_2CO_3 = 4.0 \times 10^{-8}$. An inspection of the figures shows that a solution formed from pure water and $CaCO_3$ would contain only 34 per cent. as much free CO_3 as the Ca present would represent. The remaining 66 per cent. of the CO_3 would have united with water to give HCO_3 and an equal concentration of OH. To form such a solution 16.6 mg. of $CaCO_3$ per liter of water would be required if practically complete ionization be assumed. We have calculated from the measurements of Kohlrausch[1] of the conductivity of pure water saturated with $CaCO_3$ that 12 mg. of the substance are dissolved by 1 l. of water. In so doing we have considered the hydrolysis to be 66 per cent. The agreement is only fair; the cause of the difference is not apparent.

Strontium and barium carbonates have been studied in the same way as calcium carbonate. In the case of strontium carbonate, nine experiments have been made at pressures between 0.05 and 1.1 atmospheres. The equilibrium constant $k = 1.29 \times 10^{-2}$, with an average deviation from the mean of 1.2 per cent. This value leads by Equation 7 to the solubility product $Sr \times CO_3 = k_3 = 1.567 \times 10^{-9}$. With barium carbonate, eleven experiments were made at pressures between 0.2 and 30 atmospheres. The graph for $BaCO_3$ is very similar to that for $CaCO_3$; a maximum solubility, $Ba(HCO_3)_2 = 0.028$, is reached at a concentration of $H_2CO_3 = 0.727$, corresponding to a calculated CO_2 pressure of about 22 atmospheres. The solubility of $Ba(HCO_3)_2$ is 7.3 g. per liter or 0.73 g. in 100 cc. of water. For $BaCO_3$ the equilibrium constant was found to be $k = 2.24 \times 10^{-2}$; average deviation from mean = 0.8 per cent. The solubility product $Ba \times CO_3 = k_3 = 8.1 \times 10^{-9}$.

[1] *Z. physik. Chem.*, **44**, 236 (1903).